



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :  C02F 1/28, B01J 20/16		A1	(11) International Publication Number: <b>WO 99/65826</b>  (43) International Publication Date: 23 December 1999 (23.12.99)																								
<p>(21) International Application Number: PCT/SE99/01065</p> <p>(22) International Filing Date: 15 June 1999 (15.06.99)</p> <p>(30) Priority Data: 9802140-5 16 June 1998 (16.06.98) SE</p> <p>(71) Applicant (<i>for all designated States except US</i>): ORDIO AB [SE/SE]; c/o Teknopol AB, Ideon, S-223 70 Lund (SE).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>): ERIKSSON, Håkan [SE/SE]; Borgåslängan 12, S-224 72 Lund (SE). LARSSON, Kåre [SE/SE]; Norra Villavägen 7B, S-237 34 Bjärred (SE).</p> <p>(74) Agent: AWAPATENT AB; P.O. Box 45086, S-104 30 Stockholm (SE).</p>		<p>(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.</i>  <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  <i>In English translation (filed in Swedish).</i></p>																									
<p>(54) Title: A METHOD FOR PURIFYING WATER OF PESTICIDES</p> <p>(57) Abstract</p> <p>The invention relates to a method for purifying water of pesticides and their decomposition products, and in particular to water intended to be used for human consumption or in food production. The method consists in carrying out the purification with a view to removing pesticides having a Log P value (distribution coefficient in a two-phase system of octanol-water) which is &gt; 1.5, contacting the water with a hydrophobic zeolite which has the composition <math>[(\text{AlO}_2)_x(\text{SiO}_2)_y]</math>, wherein x and y are integers and <math>y/x &gt; 15</math>, and which is directly synthesised as a hydrophobic zeolite or obtained by treating the corresponding hydrophilic zeolite in cationic form, in particular alkali metal form, preferably Na form, by means of at least two sequences of ion exchange-calcination for conversion to a hydrophobic zeolite and carrying out the purification until a total concentration of pesticides present in the water of not more than 0.5 <math>\mu\text{g/l}</math>.</p>																											
<table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Volume (mL)</th> <th>USY Concentration (ppm)</th> <th>DAY Concentration (ppm)</th> </tr> </thead> <tbody> <tr> <td>5</td> <td>1.8</td> <td>3.5</td> </tr> <tr> <td>10</td> <td>2.4</td> <td>4.5</td> </tr> <tr> <td>15</td> <td>2.9</td> <td>5.0</td> </tr> <tr> <td>25</td> <td>3.6</td> <td>5.7</td> </tr> <tr> <td>33</td> <td>4.3</td> <td>6.2</td> </tr> <tr> <td>44</td> <td>5.0</td> <td>6.9</td> </tr> <tr> <td>50</td> <td>-</td> <td>7.2</td> </tr> </tbody> </table>				Volume (mL)	USY Concentration (ppm)	DAY Concentration (ppm)	5	1.8	3.5	10	2.4	4.5	15	2.9	5.0	25	3.6	5.7	33	4.3	6.2	44	5.0	6.9	50	-	7.2
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A method for purifying water of pesticides.

Technical Field

The present invention relates to the field of water purification and more particularly to purifying water of pesticides and their decomposition products. This primarily concerns water which should be free from pesticides to be used for human consumption (drinking water) or in food production (e.g. when feeding animals or as process water in the food industry) and which originates from water supplies polluted with pesticides. The novel feature of the invention is the use of hydrophobic zeolites in this connection.

Background of the Invention

In EC Drinking Water Directive (Council of European Communities. Directive relating to the quality of water intended for human consumption. No. 80/778/EEC. 1980), the maximum acceptable concentration (MAC) of a pesticide in drinking water is set at 0.1 µg/l and at 0.5 µg/l for the total content of pesticides in the water. Today a very large number of water supplies in Europe are polluted with pesticides and the EC directives imply that the water in these supplies must be purified if the water is to be used for human consumption.

A great number of control agents (pesticides) can be detected in surface and ground water supplies, for instance, Lindane, DDT, Dimethoate, Mecoprop, Triazines (Atrazine, Simazine, Terbutylazine etc), Chloroturon, Isoproturon, 2,4-D, MCPA, Bentazon, Dichloroprop, Primicarb, dicamba, Dichlobenil and Malathion.

A great problem in removing these pesticides is due to the fact that the pesticides which occur as pollution in water supplies are present in very low concentrations in the water (however not sufficiently low for the above-mentioned purpose), and therefore an agent which is to

adsorb these substances must provide a very strong binding of the pesticides in question. Too low a binding strength results in the pesticides, which initially were adsorbed to the agent, being released and leaking out again to the water which is to be consumed. In other terms, great demands are put on agents for the purification of water for this purpose.

The agent of which practical use is made today in this connection is activated carbon, which is described, for instance, in Croll, B. Nitrate and pesticides in groundwaters in Anglian water, UK, Water, 53, 159-169, 1997.

The present invention relates to an alternative to activated carbon as adsorbent for this purpose, namely hydrophobic zeolites. Besides constituting an alternative in this application, the zeolites have also been found to yield important advantages compared to activated carbon, which will be described in more detail below.

Zeolites, which can be generally defined as aluminium silicates with spatial-reticular structure, are, of course, known per se, and as an example of literature on zeolites mention can be made of Breck, D.W. (1974) Zeolite Molecular Sieves, Wiley, New York. The term hydrophobic (ultrastable) zeolites is also generally known per se, the degree of hydrophobicity being defined by the ratio of Si/Al, wherein hydrophobic zeolites have a high silicon content and thus few structural charge carriers.

The use of hydrophobic zeolites as adsorbents for certain specific substances is also previously known. Thus US-patent specification 5,108,617 discloses the adsorption of detergents to hydrophobic zeolites, whereas WO 97/15391 discloses the adsorption of preservatives, such as phenol and cresol, from protein solutions. However, pesticides are generally composed of complex ring structures with branches, and nothing in this prior-art technique suggests that these very bulky substances could pass into the pore system of the zeolites and thus be ad-

sorbed by the zeolites with the high degree of binding kinetics (binding rate) which have been found in connection with the present invention and which are considerably greater than previously known binding rates with 5 polymeric adsorbents and activated carbon. This is also the case in comparison with the type of zeolites mentioned in WO 95/05239. This specification describes in very general terms the use of a dealuminised zeolite Y in connection with, for instance, lipophilic pesticides, but 10 the specification does not contain any results whatsoever. Moreover, the zeolite used therein has been dealuminised in a completely different way than the zeolite used according to the present invention, namely by a special  $\text{SiCl}_4$  treatment, which results in a product having a 15 completely different structure and thus entirely different qualities.

#### Description of the Invention

Thus the present invention generally relates to a 20 method for purifying water of pesticides and their decomposition products using a zeolite. The great field of application in this connection is water from water supplies, which are polluted with control agents, i.e. pesticides of different kind, and in which the water should 25 be free from pesticides to be used for human consumption or in food production (when feeding animals or as process water in the food industry). The method is characterised by carrying out the purification with a view to removing pesticides having a Log P value (distribution coefficient 30 in a two-phase system of octanol-water) which is  $> 1.5$ , contacting the water with a hydrophobic zeolite which has the composition  $[(\text{AlO}_2)_x(\text{SiO}_2)_y]$ , wherein x and y are integers and  $y/x > 15$ , and which is directly synthesised as a 35 hydrophobic zeolite or obtained by treating the corresponding hydrophilic zeolite in cationic form, in particular in alkali metal form, preferably Na form, by means of at least two sequences of ion exchange-calcination for

conversion to a hydrophobic zeolite, and carrying out the purification until a total concentration of pesticides present in the water of not more than 0.5 µg/l.

As indicated above and as will be described below in 5 more detail, a special type of hydrophobic zeolites has thus been found to be usable for the adsorption of pesticides having complex ring structures and often branches, i.e. very bulky compounds, and at a very high degree of binding kinetics. This makes the zeolites in question extremely well suited for said pesticides, since they are 10 present in very low concentrations as pollutants in water supplies and an agent which is to adsorb these substances must have a very strong binding thereto. Moreover, the very high degree of binding kinetics allows the water 15 flow which is to be purified to keep a very high flow rate compared to the adsorbent which is currently used in practice, i.e. activated carbon, which, of course, presents great advantages. Thus an example, which will be presented below, shows that a treatment of about 15 min 20 with the zeolite used according to the invention corresponds to a treatment of about 2 h with activated carbon.

Another great advantage of these hydrophobic zeolites compared to many other adsorbents is that the zeolites are inert materials resistant to heat up to about 25 1100°C. This enables the binding capacity of the zeolites to be easily regenerated by heating, so that a combustion of the material which has been adsorbed to the zeolite takes place. The high binding capacity in respect of pesticides as well as the binding rate and the possibility 30 of easy regeneration of the binding capacity make these zeolites unique in the adsorption of pesticides in water.

The zeolites used are generally of the type which corresponds to the composition  $[(\text{AlO}_2)_x(\text{SiO}_2)_y]$ , wherein x and y are integers and  $y/x > 15$ , preferably  $> 100$ , more 35 preferably  $> 200$  and often  $> 1000$ .

According to the invention, hydrophobic zeolites of the above kind are preferably selected from the group

consisting of silicalite, mordenite and zeolite Y. As a rule, the usability of the zeolites is limited by the size and accessibility of the pores in the zeolite crystals, silicalite and zeolite Y having three-dimensional pore systems, which are highly accessible, whereas the pore system in mordenite is one-dimensional and thus somewhat less accessible. As concerns the size of the pore system, both mordenite and zeolite Y belong to the zeolites having the greatest pore diameters, that is 5  $\approx 7.5 \text{ \AA}$  and  $\approx 7 \text{ \AA}$ , respectively, whereas silicalite has pore diameters (two different types of pores) of  $\approx 5.5 \text{ \AA}$ . Taken together, zeolite Y is, however, in most cases particularly preferred.

Otherwise, principles known per se are applicable to 15 zeolites. Thus, a cation can be bound to the zeolitic basic structure for each Al atom, e.g. Na. Other ions, such as P, B and Ge, can to a certain extent replace Al and Si to provide zeolitic basic structures and they can thus also be used in the method according to the invention.

20 All zeolites contain a certain amount of water molecules. Usually hydrophobic zeolites are prepared by modification of synthetically derived hydrophilic zeolites, from which a great or a small portion of the Al molecules has been removed to render the zeolite hydrophobic.

25 Zeolites having a great portion of silicon or silicon dioxide have strong hydrophobic capacities and they are stable in water-based systems within a wide pH range and also insensitive to oxidising and reducing agents. Furthermore, they resist high pressures and high temperatures without changing.

30 However, the zeolite used in the method according to the present invention can be described as follows.

According to a first alternative, it is obtained 35 from the corresponding hydrophilic zeolite in alkali metal form, preferably Na form. It appears from that mentioned above that it is a common method to remove a great or a small portion of Al molecules from synthetically

prepared hydrophilic zeolites. The important thing in this case is, however, to treat the hydrophilic zeolite, which is present in alkali metal form, by means of a series or a sequence of ion change and calcination operations so as to obtain the hydrophobic zeolite.

The actual method of preparation and the hydrophobic zeolites thus obtained have already been described in the literature, but this is not the case with the advantageous use to which the present invention relates. Thus, reference can, for instance, be made to the above-mentioned publication Breck, D.W. (1974) *Zeolite Molecular Sieves*, Wiley, New York, and in particular to the section "E. Defect Structures - Stabilization - Superstable Zeolites" at pp 507 ff. In this section, details can be found concerning preparation methods and characteristics of these zeolites, which are often referred to as ultra-stable or superstable zeolites.

From a general point of view, the preparation involves at least two sequences of ion exchange and calcination, preferably two or three, i.e. two or three ion-exchange operations and two and three calcination operations, respectively, the sequences generally ending with a calcination.

The ion exchange thus usually comprises ammonium-ion exchange and the last ion-exchange step is generally carried out with the aid of an acid to convert the zeolite to the H form.

The last calcination is preferably performed at a temperature exceeding 600°C, more preferably exceeding 700°C and most preferably in the range of 700°C-1000°C, in particular 700°C-850°C.

The preceding calcination step(-s) is/are generally carried out at a lower temperature than the final calcination, for instance, in the range of 500°C-700°C, such as 500°C-600°C.

Below follows a suitable method, described by Breck:

1. Sodium zeolite Y (hydrophilic) is subjected to ion exchange with an ammonium ion (e.g. ammonium sulfate), for instance at about 100°C, to a level exceeding 50%, e.g. 80% (equivalents NH<sub>4</sub><sup>+</sup>/total cationic equivalents).  
5
  2. The zeolite which has been ammonium-ion exchanged and contains sodium residues is heated to at least 500°C, e.g. 540°C (about 3 h), which results in a material corresponding to a regular decationised zeolite.  
10
  3. The calcinated zeolite from step 2 is treated once more with ammonium ions (e.g. ammonium sulfate), e.g. at about 100°C, for further reduction of the cationic content in question.  
15
  4. The zeolite from step 3 is calcinated at a temperature in the range of 700°C-850°C, e.g. about 815°C for 3 h.
- According to a second alternative, the hydrophobic  
20 zeolite used in the method according to the invention can, however, also be obtained by direct synthesising of a hydrophobic zeolite, i.e. without any intermediate dealuminisation from a hydrophilic zeolite. Methods for such direct synthesis are also known per se and can be  
25 used for the preparation of a hydrophobic zeolite having qualities or characteristics similar to those of the above-mentioned ultrastable or superstable zeolite.
- For instance, GB 1,117,568 thus discloses direct  
30 synthesis of a hydrophobic zeolite and details of the preparation thereof as well as such a zeolite can be retrieved from said specification.

Moreover, a common feature of the two above-mentioned alternatives concerning the zeolite which is used in the method according to the invention is that the zeolite is generally thermally stable up to 1000°C, which, for instance, can be proved by means of X-ray powder diffraction studies and/or adsorption measuring. Further-

more, it preferably contains less than 1 % by weight alkali metal (in particular Na), and more preferably less than 0.5 % by weight.

Moreover, the zeolite can be used as such or in the form of sintered zeolite crystals or in the form of crystals contained or suspended in non-zeolitic material. In addition, it can be deposited on or otherwise suitably combined with one or more, preferably permeable, non-zeolitic materials. As an example of a usable non-zeolitic material, mention can be made of agarose.

Otherwise, the chemistry of zeolites is known to the one skilled in the art and therefore a more detailed description should not be necessary. Further details of the use of zeolites for purification or adsorption purposes can thus be retrieved from prior-art, among other things, from the specifications discussed above.

The method according to the invention can in general be carried out batchwise as well as continuously or semi-continuously. According to one alternative, the hydrophobic zeolite is added directly to the solution which is to be purified, while another alternative is represented by the case in which the hydrophobic zeolite is put or packed into a column or a filter or formed to a column or a filter, through which the aqueous solution which is to be purified is allowed to pass. Different specific applications can, of course, be used, but they should not need any further presentation, as they can be retrieved from prior-art technique known per se.

The zeolites used cannot, of course, adsorb infinite amounts of pesticides, and, if action is not taken, they will eventually leak them out. However, as the zeolites are easy to regenerate by heating, a preferred embodiment of the method according to the invention involves heating of the zeolite, after the desired degree of purification, or even during the purification, to a temperature exceeding 700°C, more preferably exceeding 850°C and most preferably in the range of 900-1100°C. If possible risks of

chemical contamination and biological infection are to be eliminated as well, it is also possible to carry out the corresponding heating by pre-treating the zeolite involved. Another alternative in connection with regeneration 5 concerns the treatment of the zeolite with so-called supercritical carbon dioxide, where the supercritical carbon dioxide functions as a solvent and elution agent, the eluted substances being reusable.

As mentioned above, the method according to the invention 10 is in particular intended for the purification of water having very low concentrations of pesticides. Thus the purification is often to be carried out on water containing not more than 10 µg/l of the pesticide which is to be exposed to purification. According to the invention, 15 it has been found that it is possible to carry out a purification until a very low concentration of said pesticides, which means that the purification is performed until the total concentration of pesticides present in the water is not more than 0.5 µg/l. Each one of the pesticides is also preferably subjected to purification 20 until not more than 0.1 µg/l.

Thanks to the high degree of binding strength of the zeolites used in the method according to the invention, it is, as previously suggested, possible to use a great water flow 25 in the contact between the water and the zeolite, i.e. a short time of contact, which is preferably in the range of about ten seconds and up to 20-30 minutes or even less, such as 10 seconds-15 minutes or more preferably 20 seconds-10 minutes. Satisfactory results can often be obtained even in the range of 10 seconds-30 30 minutes.

The amount of zeolite used in relation to the volume of water which is to be purified varies with the specific pesticide which is to be removed and should thus be determined 35 by the one skilled in the art for each individual case. Naturally, it is however desirable to treat as great a volume of water as possible with as small an

amount of zeolite as possible, and thus the invention has proved to be particularly efficient in this respect. However, in the method use is generally made of 1 kg zeolite per 100 litres of water or more, preferably 1 kg zeolite 5 per 1000 litres of water or more, and more preferably 1 kg zeolite per 10,000 litres of water or more.

By means of the method according to the invention, it has thus surprisingly been found that it is possible to remove, or adsorb, pesticides having complex or bulky 10 structures and in particular with a high degree of binding kinetics. It has been found that the invention is especially interesting by allowing the removal of substances having a Log-P-value which is >1.5, preferably >2, and more preferably >2.4. Said Log-P relates to the 15 distribution coefficient of the substance in a two-phase system of octanol-water, which is a generally accepted manner of describing the qualities of a molecule. Said value can be found in the literature, and as an example reference can be made to Hansch, C., Leo, A. and Hoehman, 20 D., Exploring Qsar, Amer. Chem. Soc., 1995, Washington DC.

Furthermore, if the pesticide contains an ionisable group, the adsorption to the zeolite is stronger when the 25 pesticide is non-ionised. This can, for instance, be achieved by adjusting or regulating the pH value of the aqueous solution, so that it is preferably in the range of 1-9, and more preferably 2-9. In many cases, the pH can be adjusted to a value in the range of 1-3. In other words, this adjustment is carried out if needed, i.e. if 30 the pH initially deviates from the desired pH and/or if the pesticide contains said ionisable group (or groups).

The term pesticide is used in connection with the invention in a conventional sense, i.e. it refers to a substance or a mixture of substances intended to prevent, 35 fight, repel or alleviate the effect of an infestant (injurious animal, harmful insect, harmful plant etc). Thus

the term includes, for instance, herbicides, insecticides, fungicides, biocides, algicides etc.

In view of the good effect of the method according to the invention, in particular on bulky substances, the 5 method is, however, advantageously used for purifying water of primarily herbicides, insecticides and fungicides, in particular herbicides and insecticides.

As concrete examples of pesticides which in connection with the method according to the invention should bind 10 satisfactorily to the zeolite, mention can be made of, in particular, atrazine (6-chloro-N-ethyl-N-isopropyl-1,3,5-triazinediyl-2,4-diamine); terbutylazine (6-chloro-N-(1,1,-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine); simazine (2-chloro-4,6-bis(ethylamino)-1,3,5-triazine); chloroturon (N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea); isoproturon (N,N-dimethyl-N'-(4-(1-methyl-ethyl)phenyl)urea; MCPP (2-(2-methyl-4 chlorophenoxy)pro- 15 pionic acid); dichloroprop ( $\alpha$ -(2,4-dichlorophenoxy)pro- pionic acid); 2,4-dichlorophenoxyaceticacid); MCPA (2- 20 methyl-4-chlorophenoxyaceticacid); bentazon (3-(1-methyl-ethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide); DDT (2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane); lindane (benzenehexachloride); metoxuron (N'-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea); metamitron (4-amino-3- 25 methyl-6-phenyl-1,2,4-triazine-5(4H)-one); metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4- 30 triazine-5(4H)-one); pirimicarb (2-(dimethylamino)-5,6,-dimethyl-4-pyrimidinyldimethylcarbamate); dimetachlor (2-chloro-N-(2,6-dimethylphenyl)-N-(2-methoxyethyl)acet- 35 amide); dicamba (3,6-dichloro-2-methoxybenzoicacid); lenacil (3-cyclohexyl-6,7-dihydro-1H-cyclopentapyridine-2,4(3H,5H)-dione; chloropyriphos (0,0-diethyl O-3,5,6-trichloro-2-pyridylphosphorthioate); and meta- zachlor (2-chloro-N-(2,6-dimethylphenyl)-N-(1H-pyrazole- 1-ylmethylacetamide).

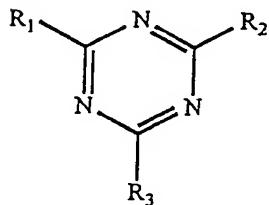
It appears from that stated above that the method according to the invention in particular allows removal

12

of heterocyclic, preferably heteroaromatic, pesticides having 1, 2 or 3 N atoms in the ring and a molecular weight of  $\geq 200$ , in particular in the range of 200-300, or aromatic compounds having a molecular weight of  $\geq 200$ , in particular in the range of 200-300. Moreover, both these groups of compounds are often halogen-substituted (halogen = F, Cl or J), in particular chloro-substituted. Another group of pesticides which are removable with the aid of the method are alicyclic compounds, in particular halogen(e.g. Cl)-substituted, and with a molecular weight of  $\geq 200$ , such as 200-300.

More specifically, interesting pesticides can be defined according to any one of the following general formulae:

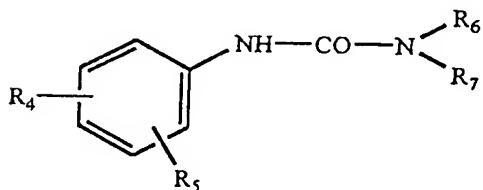
15



(I)

wherein: R<sub>1</sub> is halogen, preferably Cl,  
R<sub>2</sub> is H or -NH-(C<sub>1</sub>-C<sub>6</sub>-alkyl) and  
R<sub>3</sub> is H or -NH-(C<sub>1</sub>-C<sub>6</sub>-alkyl)

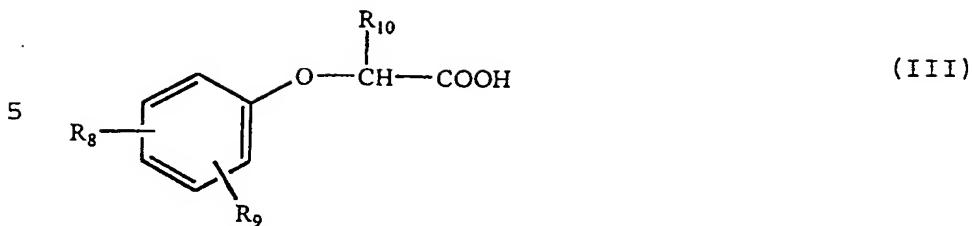
25



(II)

wherein: R<sub>4</sub> is H or halogen (preferably Cl),  
R<sub>5</sub> is H, halogen (preferably Cl) or C<sub>1</sub>-C<sub>6</sub>-alkyl,  
R<sub>6</sub> is H or C<sub>1</sub>-C<sub>6</sub>-alkyl and  
R<sub>7</sub> is H or C<sub>1</sub>-C<sub>6</sub>-alkyl

35



wherein:  $\text{R}_8$  is H or halogen (preferably Cl)  
 10         $\text{R}_9$  is H, halogen (preferably Cl) or  
 C<sub>1</sub>-C<sub>6</sub>-alkyl and  
 R<sub>10</sub> is H or C<sub>1</sub>-C<sub>6</sub>-alkyl.

In these formulae halogen is, as mentioned above, represented by fluorine, chlorine and iodine, and C<sub>1</sub>-C<sub>6</sub>-alkyl is a straight or branched alkyl group having 1-6 carbon atoms, i.e. methyl, ethyl, propyl, butyl, pentyl and hexyl (propyl up to hexyl also include normal, iso, sec and tert groups).

Furthermore, the symbols R<sub>4</sub>, R<sub>5</sub>, R<sub>8</sub> and R<sub>9</sub> can also  
 20        be present in any free position in the benzene ring.

#### EXAMPLES

The present invention will now be further elucidated by means of the following concrete examples, which are  
 25        only intended to illustrate the invention and should not be considered to restrict the scope of the invention in any respect other than that stated in the appended claims.

#### EXAMPLE 1

30        The herbicide terbutylazine was solubilised in pure water in a concentration of 1 mg/l (1ppm). The terbutylazine solution was filtrated through a column containing 1 g USY particles of a size of 63-125 µm at a flow rate of 240 ml/h. (USY= "Ultra Stable Zeolite Y" from the  
 35        Japanese company Tosoh, i.e. in accordance with the invention.) The concentration of terbutylazine in the filtrate emanating from the column was determined by

adsorption at 225 nm, the results being presented in Fig. 1.

The flow rate used in this example yielded a residence time in the column of 30 s, which was sufficient 5 for the adsorption of the specified amount of terbutylazine under the detection level.

#### EXAMPLE 2

10 The herbicide terbutylazine in an amount of 10 mg/l in pure water was incubated with different amounts of USY or activated carbon (CarboTech, Pool) for 15 minutes and 120 minutes, the results being shown in Fig. 2.

15 It appears from these results that the zeolite USY binds the pesticide considerably faster than activated carbon and that an incubation of 15 minutes with the zeolite corresponds to a 2 h incubation with the activated carbon. A short residence time of the water, i.e. a fast flow, can therefore be used with a zeolite filter 20 for the adsorption of pesticides.

#### EXAMPLE 3

Ground water from a water supply in southern Sweden 25 which was contaminated with atrazine (0.2 µg/l) was collected and pumped through a filter containing 1 g USY particles (63-125µm) at a flow rate of 240 ml/h (residence time in the filter 30 s). Fractions of 1 l were collected after the zeolite filter and the concentrations of atrazine in the fractions were analysed by an accredited laboratory (AgroLab Scandinavia AB, Box 9024, 30 291 09 Kristianstad, Sweden).

The results are presented below in Table 1.

TABLE 1

<u>Volume (l)</u>	<u>Concentration of atrazine (µg/l)</u>
1	<0.1
35 2	<0.1
5	0.2

This proves that the zeolite is efficient in the purification of ground water which is polluted with a low percentage of the pesticide atrazine with a residence time in the column of 30 s.

5

EXAMPLE 4

Affinity constants between USY and different herbicides were calculated with Scatchard plots after incubations of 15 min in ambient temperature with USY particles of 63-125  $\mu\text{m}$ . The results are shown in Table 2.

TABLE 2

Herbicide	Affinity constant $K_{aff} (\mu^{-1})$
Atrazine	$0.6 \times 10^5$
Chlorotuloron	$0.5 \times 10^5$
15 Isoproturon	$1.8 \times 10^5$
Mecoprop	$1.0 \times 10^5$
Terbutulazine	$1.7 \times 10^5$

The adsorption capacity of the zeolites depends on the binding strength between the zeolite and the pesticide, and this example illustrates the binding strength in the form of the affinity constant between a zeolite and a few pesticides (herbicides) which have all been reported as pollutants in groundwater. A zeolite filter would thus adsorb these pesticides with the same satisfactory efficiency as in the case of atrazine in Example 3.

EXAMPLE 5

A 20 ppm aqueous solution of atrazine was pumped through a filter consisting of 30 mg zeolite particles USY having a particle size of 63-125  $\mu\text{m}$ . The time of contact was 5 s and the atrazine content in the solution after the filter was determined by measuring the absorbency at 225 nm.

35 The experiment was repeated under identical conditions but with a filter consisting of particles of the zeolite DAY, which is a zeolite marketed by Degussa AG

and of the kind mentioned in WO 95/05239. In other words, the zeolite is obtained by dealuminisation of a hydrophilic zeolite by treatment with SiCl<sub>4</sub>.

5 The results from the two experiments are presented in Fig. 3. These results confirm the extraordinary binding kinetics of the zeolite used according to the invention.

EXAMPLE 6

- 10 The experiments in Example 5 were repeated but with a 100 ppm aqueous solution of 2,6-dichlorobenzamide solution. Also in this case, the time of contact was 5 s. The absorbency of the remaining 2,6-dichlorobenzamide content was measured at 220 nm.
- 15 The results are shown in Fig. 4 and again the extraordinary binding kinetics of the zeolite according to the invention are confirmed.

## CLAIMS

1. A method for purifying water of pesticides and  
5 their decomposition products using a zeolite, in particu-  
lar water from water supplies which are polluted with  
pesticides and intended to be used for human consumption  
or in food production, characterised by car-  
rying out the purification with a view to removing pesti-  
10 cides having a Log P value (distribution coefficient in a  
two-phase system of octanol-water) which is >1.5, con-  
tacting the water with a hydrophobic zeolite which has  
the composition  $[(\text{AlO}_2)_x(\text{SiO}_2)_y]$ , wherein x and y are in-  
tegers and  $y/x > 15$ , and which is directly synthesised as  
15 a hydrophobic zeolite or obtained by treating the corre-  
sponding hydrophilic zeolite in cationic form, in par-  
ticular in alkali metal form, preferably Na form, by  
means of at least two sequences of ion exchange-calcina-  
tion for conversion to a hydrophobic zeolite, and carry-  
20 ing out the purification until a total concentration of  
pesticides present in the water of not more than  
0.5 µg/l.

2. A method according to claim 1, characterised by using, as a hydrophobic zeolite, a  
25 zeolite wherein  $y/x > 100$ , preferably >200, and most  
preferably >1000.

3. A method according to any one of claims 1-2,  
characterised by selecting the zeolite from  
the group silicalite, mordenite and zeolite Y.

30 4. A method according to claim 3, characterised in that the zeolite substantially consists  
of zeolite Y.

35 5. A method according to any one of the preceding  
claims, characterised in that the hydrophobic  
zeolite is obtained by repeated sequences, preferably two  
or three, of ion exchange-calcination where the ion ex-  
change comprises ammonium-ion exchange.

6. A method according to claim 5, characterised in that the last ion-exchange step is carried out by means of acid to convert the zeolite to the H form.

5 7. A method according to any one of the preceding claims, characterised in that the last calcination is carried out at a temperature exceeding 600°C, preferably exceeding 700°C, in particular 700-1000°C, and more preferably 700-850°C.

10 8. A method according to any one of the preceding claims, characterised in that the zeolite is thermally stable up to 1000°C.

15 9. A method according to any one of the preceding claims, characterised in that the zeolite contains less than 1 % by weight, preferably less than 0.5 % by weight, alkali metal.

20 10. A method according to any one of the preceding claims, characterised in that the zeolite is used in the form of sintered zeolite crystals or zeolite crystals contained in or coated with or suspended in one or more non-zeolitic material(-s).

25 11. A method according to any one of the preceding claims, characterised in that the zeolite is packed in a column or a filter or formed to a column or a filter and the water is passed through the same.

12. A method according to any one of claims 1-10, characterised in that the zeolite is added directly to the water which is to be purified.

30 13. A method according to any one of the preceding claims, characterised in that before, during or after the purification, the zeolite is heated to a temperature exceeding 700°C, preferably exceeding 850°C, and most preferably in the range of 900-1100°C.

35 14. A method according to any one of the preceding claims, characterised in that the purification is carried out on water containing not more than

10 µg/l of the pesticide which is to be subjected to purification.

15. A method according to any one of the preceding claims, characterised in that the purification is carried out until a concentration of not more than 0.1 µg/l of each of the pesticides present.

16. A method according to any one of the preceding claims, characterised by adjusting, when needed, the pH of the water which is to be purified to a value in the range of 1-9, preferably 2-9 or 1-3.

17. A method according to any one of the preceding claims, characterised by using, in the contact of the water with the zeolite, a time of contact in the range of 10 s-15 min, preferably 20 s-10 min, e.g. 10 s-2 min.

18. A method according to any one of the preceding claims, characterised in that the purification is carried out with a view to removing pesticides having a Log P value which is >2, preferably >2.4.

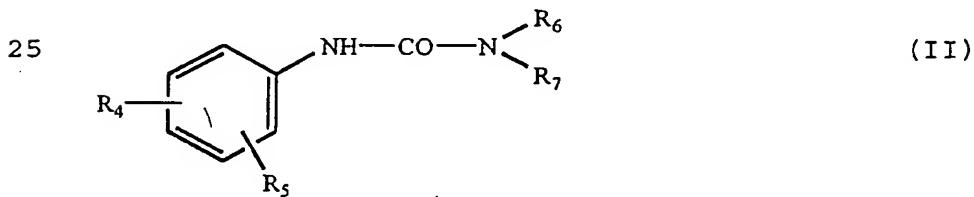
19. A method according to any one of the preceding claims, characterised in that the purification is carried out with a view to removing herbicides, insecticides and/or fungicides, in particular herbicides and/or insecticides.

20. A method according to any one of the preceding claims, characterised by removing at least one heterocyclic, in particular heteroaromatic, pesticide having 1, 2 or 3 (especially 3) nitrogen atoms in the ring and a molecular weight of ≥200, preferably in the range of 200-300.

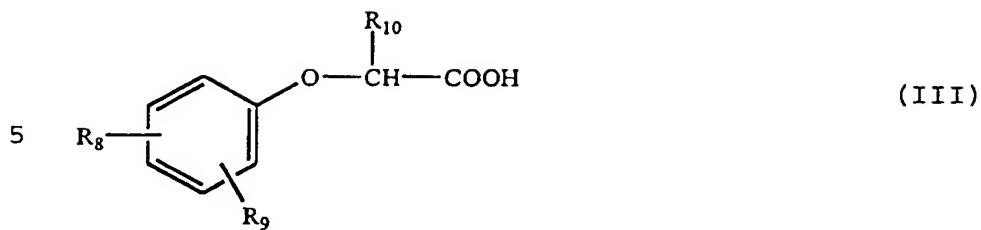
21. A method according to claim 20, characterised by removing a compound having the general formula (I)



- wherein: R<sub>1</sub> is halogen, preferably Cl,  
 R<sub>2</sub> is H or -NH-(C<sub>1</sub>-C<sub>6</sub>-alkyl) and  
 10 R<sub>3</sub> is H or -NH-(C<sub>1</sub>-C<sub>6</sub>-alkyl)
22. A method according to claim 21, characterised by removing atrazine, terbutylazine and/or simazine.
23. A method according to any one of the preceding claims, characterised by removing at least one aromatic compound having a molecular weight of >200, preferably in the range of 200-300, which compound is also preferably mono- or polyhalogen-substituted (especially chloro-substituted).
- 20 24. A method according to claim 23, characterised by removing a compound having the formula (II) and/or (III):

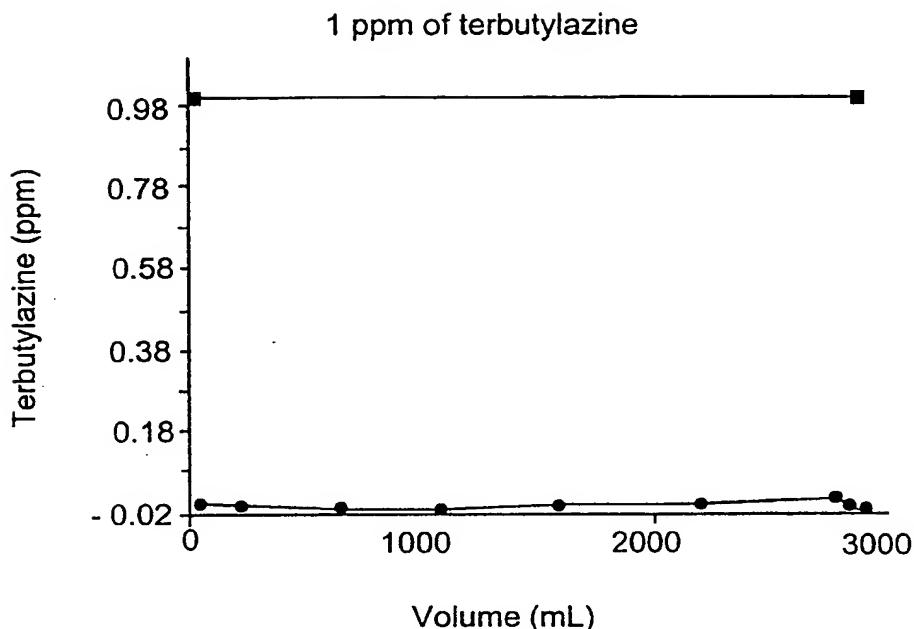
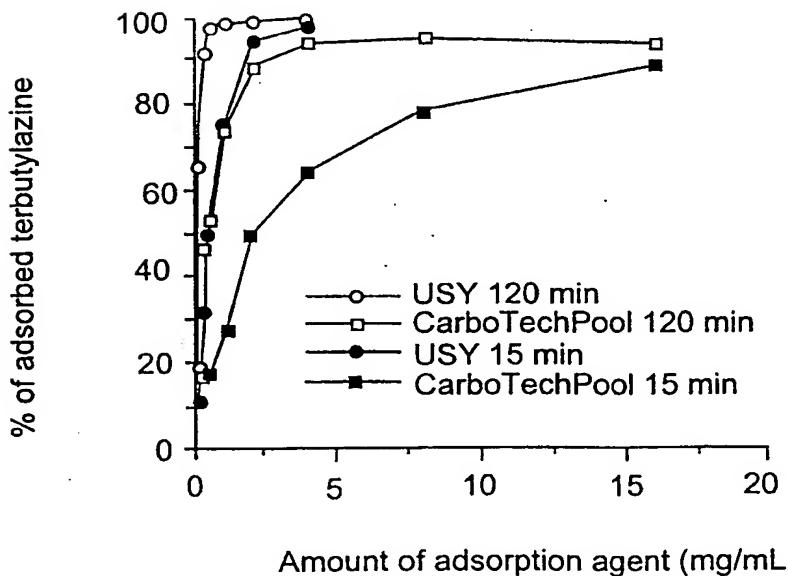


- 30 wherein: R<sub>4</sub> is H or halogen (preferably Cl),  
 R<sub>5</sub> is H, halogen (preferably Cl) or C<sub>1</sub>-C<sub>6</sub>-alkyl,  
 R<sub>6</sub> is H or C<sub>1</sub>-C<sub>6</sub>-alkyl and  
 R<sub>7</sub> is H or C<sub>1</sub>-C<sub>6</sub>-alkyl

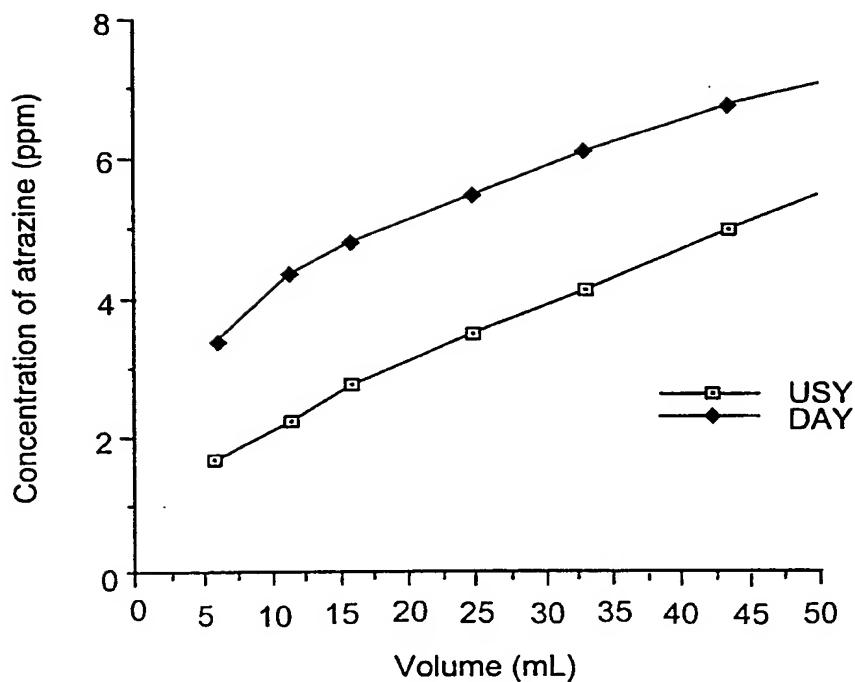
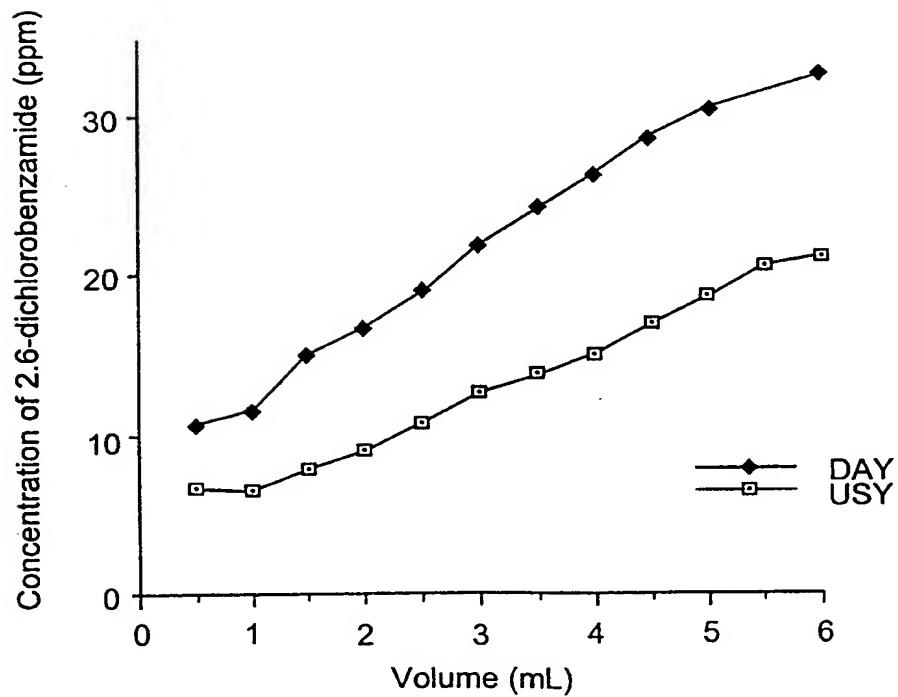


- wherein: R<sub>8</sub> is H or halogen (preferably Cl)  
 10 R<sub>9</sub> is H, halogen (preferably Cl) or  
     C<sub>1</sub>-C<sub>6</sub>-alkyl and  
     R<sub>10</sub> is H or C<sub>1</sub>-C<sub>6</sub>-alkyl.
25. A method according to claim 24, characterised by removing chloroturon, isoproturon,  
 15 MCPP, dichloroprop, 2,4-dichlorophenoxyacetic acid and MCPA.
26. A method according to any one of preceding claims, characterised by removing at least one alicyclic compound, in particular mono- or polyhalogenated (e.g. -chloro-substituted), having a molecular weight of  $\geq 200$ , in particular in the range of 200-300, preferably lindane.
27. A method according to any one of the preceding claims, characterised by removing pirimicarb,  
 25 metribuzin, chloropyriphos, lenacil, metamitron, bentazon, DDT, metoxuron, dimetachlor, dicamba and/or meta-zachlor.
28. A method according to any one of the preceding claims, characterised by using the zeolite at  
 30 a ratio of zeolite to water which is to be purified, of 1 kg zeolite per 100 litres of water or more, preferably 1 kg zeolite per 1000 litres of water or more, and more preferably 1 kg zeolite per 10,000 litres of water or more.

1/2

**Fig. 1****Fig. 2**

2/2

**Fig. 3****Fig. 4**

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/SE 99/01065

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC6: C02F 1/28, B01J 20/16**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC6: C02F, B01J**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**SE,DK,FI,NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**WPI, EPDOC, DIALOG**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9505239 A1 (WILHELM SÖNDGEN GMBH), 23 February 1995 (23.02.95), page 4, line 3 - line 7, abstract  --	1,4
A	WO 9715391 A1 (ANDERSSON, STEN ET AL), 1 May 1997 (01.05.97), claims 1,7-11,15,19  --	1-4
A	US 5108617 A (HÅKAN ERIKSSON ET AL), 28 April 1992 (28.04.92), column 3, line 37 - line 42, claims 1, 6  --	1-4

Further documents are listed in the continuation of Box C.

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**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/SE 99/01065**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 8705592 A1 (ANOX AKTIEBOLAG ET AL), 24 Sept 1987 (24.09.87), page 3, line 16 - line 19, abstract  --	1,17
A	DE 4327981 A1 (PALL CORP.), 24 February 1994 (24.02.94), page 4 - page 5  -- -----	1,19

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/SE 99/01065**

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO	9505239	A1	23/02/95	AU 7535594 A	14/03/95
WO	9715391	A1	01/05/97	AU 693047 B AU 7352496 A CA 2235767 A SE 505274 C SE 9503731 A US 5936061 A	18/06/98 15/05/97 01/05/97 28/07/97 25/04/97 10/08/99
US	5108617	A	28/04/92	SE 8902919 A	06/03/91
WO	8705592	A1	24/09/87	AU 7124787 A SE 456087 B,C SE 8601177 A	09/10/87 05/09/88 14/09/87
DE	4327981	A1	24/02/94	CA 2079820 A FR 2694928 A,B GB 2269815 A,B IT 1261242 B IT T0930624 D JP 2706658 B JP 6254546 A US 5178768 A	21/02/94 25/02/94 23/02/94 09/05/96 00/00/00 28/01/98 13/09/94 12/01/93

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